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SURFACE OPTICAL EXCITATIONS ASSOCIATED WITH CO CHEMISORPTION ON--ETC(U)  
JAN 78 G W RUBLOFF, J L FREEOUF

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SURFACE OPTICAL EXCITATIONS ASSOCIATED WITH CO  
CHEMISORPTION ON Ni(111)

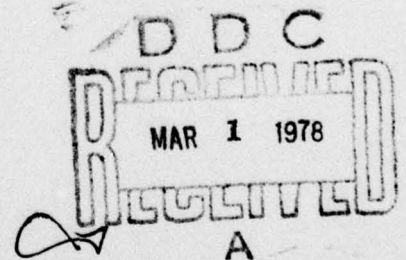
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Surface Optical Excitations Associated with CO Chemisorption on Ni(111).\*

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**ABSTRACT**

Surface optical excitations associated with CO chemisorption on Ni(111) have been studied using surface reflectance spectroscopy (SRS) and electron energy loss spectroscopy (ELS). SRS measurements using s- and p-polarized light in the photon energy range 4-35 eV are analyzed using a simple dielectric model to deduce surface optical transitions. A comparison of the SRS and ELS results for CO/Ni(111) with the optical excitations in gas and solid phase CO and in transition metal carbonyls reveals correlations in spectral structure which are used as a basis to suggest possible identifications of the surface optical transitions; these include charge transfer excitations from the metal to the CO ( $2\pi^*$ ) affinity level at  $\sim 6$  eV, singlet valence transitions  $X^1\Sigma^+ \rightarrow A^1\Pi$  ( $5\sigma \rightarrow 2\pi^*$ ) of the chemisorbed CO molecule near  $\sim 8$  eV, and Rydberg excitations of the CO orbitals near 13 eV and above.

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## I. Introduction

The chemisorption of CO on transition metal surfaces has been the subject of intense study for some time. There is considerable interest in this system because (i) CO is a small molecule which chemisorbs associatively, so that it should present one of the most straightforward systems for fundamental experimental and theoretical investigations of molecular chemisorption, and (ii) CO chemisorption plays a significant role in a number of important catalytic reactions, such as methanation, methanol synthesis, Fischer-Tropsch synthesis, and CO oxidation.

In the past several years many new tools of surface analysis have been applied to the problem of CO chemisorption on transition metal surfaces. In particular, recent ultraviolet photoemission spectroscopy studies<sup>1-11</sup>, including angle-resolved<sup>4-9</sup> and photon energy dependent measurements<sup>9-11</sup>, have provided much information about the occupied density of electron states at the surface, while electron energy loss spectroscopy (ELS) has begun to reveal some characteristic excitations of the surface electronic structure<sup>12-14</sup>.

In this paper we report the results of surface reflectance spectroscopy (SRS) studies of CO chemisorption on Ni(111) from the near ultraviolet into the vacuum ultraviolet region of the optical spectrum. This represents the first SRS investigation of the valence electronic excitations of a molecule chemisorbed on a surface and an extension of previous SRS studies<sup>15-17</sup> into the vacuum ultraviolet region. In contrast, optical excitations investigated in earlier SRS work involved only chemisorption-induced changes in the dielectric response of the substrate. The purpose of the present work is to attempt to identify the nature of optical excitations involving electronic states of the chemisorbed molecule and to try to gain new information about the surface electronic structure. For this purpose, we also report the results of electron energy loss spectroscopy (ELS) studies of CO on Ni(111) and their comparison to the SRS results.

CO chemisorption on transition metal surfaces is generally believed to involve interaction of both the highest-lying filled CO orbital ( $5\sigma$ ) and the lowest-lying empty CO orbital ( $2\pi^*$ ) with primarily the metal d-electrons<sup>18-24</sup>, as indicated schematically in Fig. 1. As expected on simple theoretical grounds, the chemisorbed CO molecule stands up normal to the surface with the carbon end closest to the metal<sup>4,6,9</sup>. Ultraviolet photoemission spectroscopy (UPS) studies have shown that the  $5\sigma$  orbital undergoes a relative shift (increase) in binding energy toward that of the  $1\pi$  orbital when the molecule is chemisorbed on a transition metal surface<sup>1-3</sup> or when it is bonded to a metal atom in a transition metal carbonyl<sup>25</sup>; this relative shift is taken as evidence for direct interaction of the  $5\sigma$  orbital in bonding. Since the "back-bonding", i.e.  $2\pi^* - d$ , interaction may also be significant,<sup>19,21-23</sup> a shift of the  $2\pi^*$  orbital (upwards in the simplest physical picture of the electronic ground state) would be expected.

In the present work we are interested primarily in three types of optical excitations involving molecular orbitals of the chemisorbed molecule. These are depicted schematically in Fig. 1. Valence excitations (V) from the molecular ground state excite electrons into higher valence orbitals. Rydberg-like transitions (R) produce excited electrons in bound hydrogenic-like orbitals of the entire molecule or in the corresponding ionization continuum. Charge-transfer excitations (CT) couple metal and adsorbate states in both directions. Because the adsorbate states are significantly localized, optical excitations associated with the chemisorbed molecule will not be simple one-electron transitions. For example, valence transition energies will not correspond to orbital energy differences in the ground state. Charge transfer excitations from filled metal states into empty adsorbate states will involve the affinity levels (AFF) of the molecule (e.g.  $2\pi^*_{\text{AFF}}$ ), which in general have similar symmetry but should have very different binding energy relative to the vacuum level from their counterparts reached by intramolecular optical transitions (e.g. by  $5\sigma \rightarrow 2\pi^*$ ). Finally, we note that excitations of the surface electronic structure of the metal may also contribute to the observed spectral features.

## II. Experimental Techniques



The measurements were carried out using two different experimental systems in order to cover different portions of the optical spectrum. The first set of measurements was made below  $\hbar\omega \approx 10$  eV photon energy using conventional light sources, while the second set was obtained over the range  $6 < \hbar\omega < 35$  eV using synchrotron radiation. For convenience we shall refer to these two sets of data as the low energy and high energy measurements respectively. Because chemisorption-induced reflectance changes are small ( $|\Delta R/R| \sim 1\%$ ), the relative reflectance must be obtained with a high stability ( $\sim 0.1$ - $0.2\%$ ).

In the low energy measurements ( $\hbar\omega < 10$  eV), a double-beam/chopper technique was used to obtain a stable measurement of the reflected light from the sample normalized to the incident light intensity. Unpolarized light from a Hinteregger-type hydrogen discharge lamp modified for hot-filament operation<sup>26</sup> was dispersed by a McPherson 218 vacuum ultraviolet monochromator. A chopped double-beam optical system was arranged in a vacuum mirror box using Al/MgF<sub>2</sub>-coated toroidal and plane mirrors, a MgF<sub>2</sub>-plate beamsplitter, and a Bulova tuning-fork chopper (frequency  $\sim 40$  Hz). In this configuration the periodic photomultiplier signal measured alternately the sample beam, reference beam, and dark current intensities, which were extracted using, sample-and-hold (boxcar integration) techniques<sup>27</sup>. The relative reflectance was obtained with a digital voltmeter and was typically stable over  $\sim 10$ - $15$  min. to  $\sim \pm 5 \times 10^{-4}$  to  $\pm 3 \times 10^{-3}$ , depending primarily on the light intensity at the particular photon energy. The vacuum in the mirror box ( $\sim 10^{-7}$  torr) was separated from that in the sample chamber ( $\sim 10^{-10}$  torr) by a bakeable MgF<sub>2</sub> window on the latter. Because of the position of the sample in the ultrahigh vacuum (UHV) chamber ( $\sim 4$ " from the sides) and the focal lengths of available toroidal mirrors, reflectance measurements were restricted to near-normal incidence, i.e. only s-polarized light.

The high energy measurements ( $6 < \hbar\omega < 35$  eV) were carried out using polarized synchrotron radiation from the 240 MeV electron storage ring at the University of Wisconsin Synchrotron Radiation Center. The radiation was dispersed by a McPherson 1.0 m UIIV

Seya-Namioka monochromator and then struck the sample, which was mounted on a manipulator to allow the angle of incidence of the light to be changed. The reflected beam intensity was measured using the total photoyield from two Au-coated photodiodes (biased at -40 V) which were positioned in the sample chamber to intercept the reflected beam for (i) incident light at near-normal incidence and (ii) p-polarized light at  $\theta_i \cong 50^\circ$  angle of incidence. Measurements in the p-polarized configuration were also obtained using a photomultiplier to sense the visible fluorescence caused by the reflected beam's hitting a sodium salicylate layer on the inside of a bakeable glass window on the UHV system. The polarization of the light beam incident on the sample was  $\sim 80\%$ . In all three cases the reflected light intensity was normalized to the photoyield from a Au wire mounted inside the monochromator near the exit slit, which served as a monitor of the incident light intensity. The relative reflectance with this normalization procedure was typically stable over  $\sim 10$  min. to  $\sim \pm 2 \times 10^{-3}$ .

For a chemisorbed molecule oriented in a particular way on a surface, one would like to know which optical transitions are excited by A-vector components of the light parallel ( $A_{\parallel}$ ) vs. perpendicular ( $A_{\perp}$ ) to the surface. Only  $A_{\parallel}$  components are present for near-normal incidence measurements. Since this is also true for the case of s-polarized light (A-vector normal to the plane of incidence) at oblique incidence, we will refer to the near-normal incidence results as s-polarized spectra (at  $\theta_i \cong 0^\circ$ ). In contrast, measurements with p-polarized light (A-vector in the plane of incidence) involve both  $A_{\parallel}$  and  $A_{\perp}$  components (approximately equal in magnitude at  $\theta_i \cong 50^\circ$ ).

The SRS data was obtained in the following way. First the "relative" reflectance spectrum, as previously described, was measured for the atomically clean Ni(111) surface by taking data at equally-spaced wavelength intervals directly into the computer via a device coupler<sup>28</sup>. Then the sample was exposed to the adsorbate gas and the relative reflectance spectrum of the CO-covered surface was recorded in the same way. The spectrum of chemisorption-induced relative changes in optical reflectance  $\Delta R/R(h\nu)$  was then calculated as



$\Delta R/R = (R_{\text{covered}} - R_{\text{clean}})/R_{\text{clean}}$ . In most cases, two clean- and then two covered-surface spectra were measured in order to distinguish any spurious noise effects which might contribute to a single  $\Delta R/R(\hbar\omega)$  spectrum. The high energy spectra obtained at higher photon energy using synchrotron radiation were corrected for second-order effects from the grating by subtracting an approximate second-order contribution to the measured relative reflectance spectra before calculating  $\Delta R/R$ . This correction was particularly important for the s- and p-polarized data obtained with the Au photodiode detectors (photoemission threshold at  $\hbar\omega \sim 6$  eV); in these cases, several model second-order corrections were computed and the spectra were terminated at a lower limit  $\hbar\omega = 8.7$  eV, above which the spectral shape was insensitive to the details of the second-order correction. In the case of the p-polarized data obtained with sodium salicylate photomultiplier detection, the spectra were terminated at a lower limit  $\hbar\omega = 5.0$  eV on account of second-order effects.

The samples were single crystals of Ni oriented with their surfaces within  $1/2^\circ$  of the (111) crystal plane. They were cleaned by a combination of  $\text{Ar}^+$  sputtering, annealing, and oxidation treatments. Surface cleanliness was monitored by ultraviolet photoemission spectroscopy. Operating pressures in the UHV system containing the sample were  $1-2 \times 10^{-10}$  torr in both the low and high energy measurements.

Electron energy loss spectroscopy measurements were made using electrons near grazing incidence ( $\sim 70^\circ$  angle of incidence) with various primary beam energies from 50-300 eV. The energy distribution of scattered electrons was obtained using a double-pass cylindrical mirror analyzer in fixed pass mode in conjunction with electron counting techniques without differentiation. Photoemission was used to check that electron beam damage to the chemisorbed CO layer was negligible.

### III. SRS: Results and Dielectric Analysis

The relative change in optical reflectance  $\Delta R/R$  caused by CO chemisorption on Ni(111)



at 300 K is shown in Fig. 2. The CO exposure used,  $\sim 5$  L ( $1 \text{ L} = 10^{-6}$  torr-sec), corresponds to approximately the saturation CO coverage at 300 K. The spectra shown have been corrected for second-order effects as explained earlier. The p-polarized spectrum (solid curve), taken at  $50^\circ$  angle of incidence with light polarized primarily ( $\sim 80\%$ ) in the plane of incidence, represents a synthesis of the high energy results obtained with the sodium salicylate/photomultiplier and the Au photodiode detectors. The s-polarized spectrum above  $\sim 9$  eV (dashed curve) was taken with synchrotron radiation and a Au diode detector, while the s-polarized spectrum at lower energy was obtained using the  $\text{H}_2$  discharge lamp and sodium salicylate/photomultiplier detection. Although the low and high energy measurements for s-polarized light (obtained in two separate experimental systems) show a significant zero-shift inconsistency, their spectral shapes - on which the following analysis primarily depends - are similar in the region near 9 eV where their energy ranges overlap.

The strongest feature in the  $\Delta R/R$  spectra is a peak  $\sim 5$  eV wide near  $\hbar\omega = 24$  eV which appears for both s- and p-polarizations. A sharper ( $\sim 2$  eV wide) peak near  $\hbar\omega = 9.5$  eV is seen in the p-polarized and in the s-polarized spectra shown in Fig. 2. A weaker shoulder-like feature is present near 14.5 eV but its shape is very different for the two polarizations.

In order to deduce chemisorption-induced changes in the surface dielectric response from the measured  $\Delta R/R$  spectra, we adopt the simple classical model of McIntyre and Aspnes<sup>29</sup> as modified to include the possibility of changes in the substrate dielectric response near the surface<sup>15</sup>. In this model the surface region (which may include substrate as well as adsorbate layers) is treated as an isotropic, uniform layer of (sub) monolayer thickness  $d$  ( $\ll \lambda$ , the wavelength of the light) having complex dielectric function  $\hat{\epsilon}^s = \epsilon_1^s + i \epsilon_2^s$ , and the bulk complex dielectric function of the substrate is  $\hat{\epsilon}^b = \epsilon_1^b + i \epsilon_2^b$ . For chemisorption-induced changes  $\Delta \hat{\epsilon}^s$  in  $\hat{\epsilon}^s$  in the limit  $d \ll \lambda$ , the relative reflectance change for s-polarized light

then becomes:

$$\left( \frac{\Delta R}{R} \right)_s = \frac{8\pi d \cos \theta_i}{\lambda} \operatorname{Im} \left( \frac{\Delta \hat{\epsilon}^s}{1 - \hat{\epsilon}^b} \right) \quad (1)$$

where  $\operatorname{Im}$  denotes imaginary part. This can be simplified to

$$\left( \frac{\Delta R}{R} \right)_s = - \frac{8\pi d \cos \theta_i}{\lambda} \left[ \frac{\epsilon_2^b \Delta \epsilon_1^s - (\epsilon_1^b - 1) \Delta \epsilon_2^s}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2} \right] \quad (2)$$

For p-polarization the result is somewhat more complicated:

$$\left( \frac{\Delta R}{R} \right)_p = \frac{8\pi d \cos \theta_i}{\lambda} \operatorname{Im} \left[ \left( \frac{\Delta \hat{\epsilon}^s}{1 - \hat{\epsilon}^b} \right) \left( \frac{1 - \frac{\Delta \hat{\epsilon}^s + 2\hat{\epsilon}^b}{(\Delta \hat{\epsilon}^s - 1)\hat{\epsilon}^b} \sin^2 \theta_i}{1 - \frac{1 + \hat{\epsilon}^b}{\hat{\epsilon}^b} \sin^2 \theta_i} \right) \right] \quad (3)$$

Two obvious and fundamental questions arise concerning the validity of this dielectric model. First, oriented molecules chemisorbed on a surface are likely to produce anisotropies in the optical response of the surface region, particularly in the vacuum ultraviolet region where excitations of the adsorbed molecule lie. In principle, any such anisotropy will appear in the dielectric analysis as differing strengths of particular optical transitions for s- vs. p-polarized spectra.

Second, one might question whether the simple classical dielectric model outlined above can describe the actual microscopic, probably nonlocal, dielectric response of a surface layer a few Å thick. Calculations by Feibelman<sup>30</sup> of the full nonlocal dielectric response at a jellium surface show that the classical model is valid for s-polarized light if the effective surface dielectric functions in eqs. (1) - (3) are defined in the most natural way in terms of the microscopic nonlocal response. However, Feibelman also shows<sup>30</sup> that surface charge

contributions which arise from the component of the photon A-vector normal to the surface make the classical model invalid (at least in principle) for the case of p-polarized light. The magnitude of such surface charge effects in  $\Delta R/R$  spectra has not been estimated theoretically for realistic systems. However, the similarities between spectral structures in  $\Delta R/R$  ( $\hbar\omega$ ) for s- and p-polarized light seen in Fig. 2 and also observed for simple gases on the low index planes of  $W^{17}$  suggest that the surface charge contributions to  $(\Delta R/R)_p$  may not be large. We therefore proceed to analyze the data on the basis of the classical model with these two caveats in mind.

The simple model (eqs. 1-3) prescribes three unknowns to be determined from a single  $\Delta R/R$  measurement:  $d$ ,  $\Delta\epsilon_1^s$ , and  $\Delta\epsilon_2^s$ . Since the surface layer thickness  $d$  enters only as a simple scale factor, we assume an arbitrary value  $d = 2 \text{ \AA}$  and seek to deduce  $\Delta\epsilon_1^s$  and  $\Delta\epsilon_2^s$ . Although both of these functions can in principle be determined by Kramers-Kronig analysis with the broad photon energy range of these measurements, this procedure can be done analytically only for s-polarized light, and in this case it often encounters convergence problems<sup>16</sup>.

Instead, we deduce  $\Delta\epsilon_1^s$  and  $\Delta\epsilon_2^s$  from the  $\Delta R/R$  by an oscillator-fitting scheme previously employed<sup>15</sup>. In this approach  $\Delta\epsilon^s$  is assumed to be the sum of several Lorentzian oscillators whose parameters are adjusted so as to reproduce the measured  $\Delta R/R$  spectrum. Results of this procedure have been found to agree with those determined by Kramers-Kronig analysis<sup>16</sup>. The optical constants  $\epsilon_1^b$  and  $\epsilon_2^b$  of the underlying bulk Ni substrate were taken from Vehse and Arakawa<sup>31</sup> in the range of their measurements 3.5 - 22 eV, while outside this range we used the values of Moravec et. al.<sup>32</sup> scaled by a multiplicative factor of order  $\sim 0.8$  to smoothly join the Vehse and Arakawa data.

It is important to emphasize that the spectral structure in  $\Delta R/R$  ( $\hbar\omega$ ) for CO/Ni(111) (Fig. 2) arises from chemisorption-induced changes in the surface optical response ( $\Delta\epsilon^s$ ). Eq's. 1-3 show that such structure in  $\Delta R/R$  ( $\hbar\omega$ ) could in principle be caused by spectral



features in  $\hat{\epsilon}^b(\hbar\omega)$ , the bulk optical constants of the substrate. However, a structureless  $\Delta\hat{\epsilon}^s$  (e.g., a transparent overlayer with  $\Delta\epsilon_1^s = \text{constant}$  and  $\Delta\epsilon_2^s = 0.0$ ) and the optical constants  $\hat{\epsilon}^b$  of Ni predict a less structured  $\Delta R/R(\hbar\omega)$  spectrum from eq's. 1-3 than is observed in Fig. 2.

2. We conclude that the structure in  $\Delta R/R(\hbar\omega)$  arises from chemisorption-induced changes in surface optical transitions, which appear in the  $\Delta\hat{\epsilon}^s(\hbar\omega)$  spectrum deduced from the dielectric analysis outlined above.

The results of this analysis for s- and p-polarized light are shown in Fig. 3, which gives  $\Delta\epsilon_2^s(\hbar\omega)$  as derived from the oscillator fit for  $d = 2\text{\AA}$ . Peaks in this function indicate new optical transitions characteristic of the surface region and induced by the CO chemisorption. The p-polarized spectrum is dominated by a peak  $\sim 2\text{ eV}$  wide near  $\hbar\omega = 6\text{ eV}$ , with an additional shoulder on the high energy side near 8 eV. These features seem to be replicated in the s-polarized spectrum as well. However, the zero-shift uncertainty in the s-polarized  $\Delta R/R(\hbar\omega)$  spectra (see Fig. 2) leads to an uncertainty in the relative magnitudes of the 6 and 8 eV features (as indicated by the dotted portion of the dashed curve in Fig. 3) and prevents us from drawing any conclusions about the polarization-dependence of the magnitudes of the 6 and 8 eV features, i.e. about optical anisotropy or surface charge effects in this region. Another peak appears near  $\hbar\omega = 13\text{ eV}$  in the s-polarized spectrum (Fig. 3), followed by a broad tail at higher energy which extends to  $\sim 20\text{ eV}$ . Related structure is seen in the p-polarized result. The sharper part of the structure, near 13 eV, seems weaker for p-polarization.

#### IV. Electron Energy Loss Spectroscopy Results

The ELS spectra for the clean and CO-covered Ni(111) surface are shown in Fig. 4 for measurements with a primary beam energy  $E_p = 250\text{ eV}$ . The shape of the spectra was found to be essentially independent of  $E_p$  over the range investigated  $50 \leq E_p \leq 300\text{ eV}$ . Structures above 2 eV in the clean surface spectrum are in close agreement with those which appear in

the volume and surface energy loss functions,  $-\text{Im}(1/\hat{\epsilon})$  and  $-\text{Im}(1/(\hat{\epsilon}+1))$  respectively, calculated from the optical constants of Ni<sup>31,32</sup>. The clean surface ELS spectrum resembles the spectrum of the surface loss function somewhat more closely than that of the volume loss function. As seen in the difference curve, i.e. CO-covered spectrum minus clean spectrum, CO chemisorption produces new ELS transitions at  $\sim 6.5$  eV and 14 eV, in agreement with previous work by Christmann et. al.<sup>14</sup> Energy losses near  $\sim 5-6$  eV and 13.5-14. eV appear to be common for chemisorbed CO on a variety of transition metal surfaces<sup>12</sup>. As compared to the usual derivative spectra for ELS measurements on surfaces, the direct ELS difference curve in Fig. 4 provides a convenient spectrum for comparison to the SRS results and to the ELS spectra of the CO molecule itself. We note in particular that the ELS features at  $\sim 5-6$  eV and  $\sim 13.5 - 14.$  eV appear to have counterparts at about the same energies in the SRS spectra in Fig. 3, although the ELS results show no feature corresponding to the shoulder near  $\sim 8$  eV in the SRS results.

## V. Discussion

### A. Optical Excitations of Molecular CO

In order to discuss the origin of structures in the SRS (Fig. 3) and in the ELS (Fig. 4) spectra for CO chemisorbed on Ni(111), these results are compared to the ELS spectra of molecular CO in the gas and solid phase<sup>33</sup> CO in Fig. 5. Peaks in the ELS spectra (in  $-\text{Im}(1/\hat{\epsilon})$ ) of molecular CO occur at essentially the same energies as peaks in the optical absorption spectra<sup>34-37</sup>.

The lowest-lying strong excitation in the ELS and optical absorption spectra of gas phase CO (Fig. 5e) appears at  $\sim 8.2$  eV. This is the first singlet valence excitation  $X^1\Sigma^+ \rightarrow A^1\Pi$  of the molecule<sup>33-35</sup>, which corresponds in a one-electron description to an excitation from the highest-lying occupied orbital ( $5\sigma$ ) to the lowest-lying empty orbital ( $2\pi^*$ ), as indicated by the



valence (V) transition in Fig. 1. The spectra at higher energy are complicated and are believed to involve primarily Rydberg excitations of the molecule<sup>33-36</sup>, near 11 eV and higher, which converge to the  $5\sigma$ ,  $1\pi$ , and  $4\sigma$  ionization limits shown from left to right in Fig. 5f. Valence excitations other than  $X^1\Sigma^+ \rightarrow A^1\Pi$  may be present as well above  $\sim 9$  eV, but these<sup>37</sup> are usually believed to be weaker in this region than the Rydberg excitation<sup>33-36</sup>.

The ELS spectrum of solid CO<sup>33</sup> (Fig. 5d) resembles quite closely that of gas phase CO except for an overall broadening of vibrational fine structure in the solid phase. It is noteworthy that the oscillator strength of Rydberg transitions at 11 eV and above in the gas phase is not shifted in energy or disturbed very much in the solid phase; this similarity will be discussed in more detail in Section V D.

#### B. Charge-Transfer Excitations for CO/Ni(111)

The strong peak which occurs near 5-6 eV in the ELS spectra for chemisorbed CO on transition and noble metals, like that seen in Fig. 5b for CO/Ni(111), has been attributed to charge transfer (CT) excitations from the filled metal d-bands to the empty CO ( $2\pi^*$ ) orbital<sup>12</sup>. This assignment is based on the analogy to and theoretical analysis of peaks in the optical absorption spectra of transition metal carbonyls which appear at energies below the first singlet valence excitation of CO. The CT transition is considered to be (filled d)  $\rightarrow 2\pi^*$  rather than  $5\sigma \rightarrow$  (empty d) since the d-band of the group VIII transition metals and of the noble metals is almost or completely full. The d  $\rightarrow 2\pi^*$  CT transition must involve electron donation into the affinity level ( $2\pi^*_{\text{AFF}}$ ) of the chemisorbed CO molecule, as depicted schematically by the CT transition in Fig. 1.

Because the strongest SRS peak, near 6 eV, appears at essentially the same energy as the ELS CT peak, we identify it as the Ni(3d)  $\rightarrow$  CO( $2\pi^*$ ) charge transfer transition. One might anticipate in a very simple picture that CT excitations between an adsorbed molecule and a semi-infinite metal surface would have significant dipole oscillator strength only for A-vector



components perpendicular to the surface (i.e. excited by p-polarized but not s-polarized light). However, the charge density of the Ni d-states at the surface is distributed in lobes which point out from the surface in different directions; depending on the local bonding site of the molecule and its spacing relative to the outer layer of surface Ni atoms, CT transitions may be excited by A-vector components parallel to the surface as well. This may explain why the CT transition is seen in the SRS results for s-polarized light (A-vector components only parallel to the surface) as well as for p-polarized light.

### C. Intramolecular Valence Excitations of Chemisorbed CO

Both the shoulder in the SRS spectra near 8 eV and the broader feature from ~ 13 eV to 20 eV appear to correspond to transitions at nearly the same energies in the ELS spectra for gas and solid phase CO. If this correlation is meaningful, then the shoulder at ~ 8 eV in the SRS spectra (Fig. 5a) may be identified as the first singlet valence excitation  $X^1\Sigma^+ \rightarrow A^1\Pi$  of the chemisorbed CO molecule.  $\Sigma \rightarrow \Pi$  excitations of a linear molecule are dipole allowed only for A-vector components perpendicular to the axis of the molecule<sup>38,39</sup>. Since CO is bonded to transition metals with its axis perpendicular to the surface<sup>4,6,9</sup>, we would expect the first singlet excitation to appear in both s- and p-polarized SRS measurements (more intense in the former). The 8 eV shoulder seems to be present in the SRS data for both polarizations, but comparison of intensities for the two polarizations is not reliable due to the uncertainties already discussed in relation to Fig. 3. Since ELS measurements are sensitive mainly to those dipole excitations of an oriented, adsorbed molecule which are polarized perpendicular to the surface<sup>40,41</sup>, one would not expect to readily observe the first singlet excitation of chemisorbed CO on transition metals in the ELS spectra<sup>39</sup>. In fact, no ELS transition is seen near 8 eV in Fig. 5b<sup>42</sup>.

Ultraviolet photoemission measurements of chemisorbed CO<sup>1-11</sup> (as well as other molecules) on metal surfaces have shown that the essential character of the electronic structure of the CO molecule is preserved in the chemisorbed phase. The initial and final states for the

valence electronic transitions of the chemisorbed molecule are thus considerably localized. As a result, the valence excitation energies are not given simply by the energy difference between empty (virtual) and filled one-electron orbitals in the ground state of the chemisorption system, either in the Hartree-Fock<sup>42</sup> or in the local density<sup>43</sup> picture. One must take into account additional effects, particularly the "self-Coulomb interaction"<sup>21,42,44</sup>: the electron excited into the  $2\pi^*$  orbital from the  $5\sigma$  feels Coulomb repulsion from only one electron remaining in the  $5\sigma$  orbital, whereas a test charge in the  $2\pi^*$  orbital (which gives the energy of the empty (virtual)  $2\pi^*$  orbital in the ground state) senses Coulomb repulsion from both electrons in the filled  $5\sigma$  orbital.

The influence of these effects in free molecules is very strong<sup>21,42-44</sup>. For example, although Hartree-Fock calculations of the  $X^1\Sigma^+$  ground state of the CO molecule give a  $5\sigma - 2\pi^*$  energy separation of 22.3 eV, excited state calculations which include the self-Coulomb interaction give much lower values<sup>44</sup> for the singlet ( $A^1\Pi$ ) and triplet ( $a^3\Pi$ ) transition energies which are close to the experimentally observed values of 8.07 and 6.04 eV respectively<sup>46</sup>.

The only theoretical estimate presently available for the first valence transition energies for chemisorbed CO comes from the calculations of Doyen and Ertl<sup>21</sup>, which include the self-Coulomb interaction. They find the singlet and triplet excitation energies of CO on Ni(110) to be 7.5 and 5.4 eV respectively. This singlet excitation energy in chemisorbed CO is in close agreement with the value  $\sim 8$  eV suggested by the analysis of the SRS data given above. Thus the results of Doyen and Ertl provide support for the interpretation of the 8 eV structure in the SRS spectra as the first singlet valence excitation of the chemisorbed CO molecule on Ni(111).

The relevance of photoemission observations and most theoretical calculations to the interpretation of valence transition energies for chemisorbed CO is unclear for two reasons. First, and most important, theoretical calculations (except for that of Doyen and Ertl) have addressed only the ground state of the chemisorption system and give no indication of how



chemisorption affects the strong correlation effects which accompany the valence excitations. This underscores the need for further calculations of electronic excited states in order to compare to experimental measurements of transition energies. Second, even the predictions of how the  $5\sigma$ - $2\pi^*$  ground state energy separation changes upon chemisorption are not completely clear. Theoretical calculations<sup>18-20,22-24,47</sup> and simple theoretical models<sup>19</sup> predict that the  $5\sigma$  orbital is shifted to lower energy (toward the  $1\pi$  and  $4\sigma$  orbitals) upon chemisorption; this is substantiated by ultraviolet photoemission measurements<sup>1-11</sup>, although the contribution of extramolecular relaxation/polarization shifts<sup>2,48</sup> to the photoemission spectrum for chemisorbed CO is not certain<sup>49</sup>. Calculations are not in agreement on whether the ground state position of the empty  $2\pi^*$  orbital is shifted up or down due to chemisorption<sup>19,20</sup>.

#### D. Rydberg Excitations of Chemisorbed CO

The broad SRS structure near  $\sim 13$  eV which extends toward higher energy to  $\sim 20$  eV resembles in an overall view the broad structure in the ELS and optical absorption spectra of gas and solid phase CO and correlates fairly well with the 14 eV structure in the ELS difference spectrum for CO/Ni(111). This correspondence suggests that the SRS and ELS structures near 13-14 eV for chemisorbed CO in Figs. 5a and 5b are associated with the Rydberg transitions which dominate the optical spectra of gas phase CO in this region. Rydberg states are excited states involving an appreciable admixture of atomic orbital components having principal quantum number greater than that of the valence shell of the molecule<sup>50</sup>; highly excited Rydberg states have hydrogenic character and radii large cf. molecular dimensions.

Although one might expect Rydberg states of free molecules to be significantly altered by the surrounding environment in a condensed phase, the oscillator strength associated with Rydberg transitions near 11-15 eV in CO seems not to be significantly disturbed in either solid or chemisorbed CO. This can be understood in the following way. First, the charge density of these low-lying Rydberg states is not very delocalized compared to the spatial extent of valence molecular orbitals. A reasonably good description of these Rydberg states is obtained



by adding only atomic 3s and 3p functions to the 1s, 2s, and 2p functions which comprise the valence states<sup>50</sup>, and radii of the atomic 3s and 3p functions<sup>51</sup> ( $\sim 1.4 \text{ \AA}$ ) are not much larger than characteristic dimensions of the molecule (the  $\text{C}\equiv\text{O}$  bond length is  $1.128 \text{ \AA}$ ). Furthermore, these radii are significantly smaller (by  $> 2X$ ) than the CO-CO intermolecular spacing for chemisorbed CO on Ni(111) ( $4.3 \text{ \AA}$  for the  $\sqrt{3} \times \sqrt{3}/R 30^\circ$  structure<sup>14</sup>) or for solid CO ( $4.0 \text{ \AA}$ <sup>52</sup>). These low-lying Rydberg states of the CO molecule thus have appreciable valence character and are rather compact spatially (cf. higher-lying, hydrogenic Rydberg states), so that they may not be grossly altered by the molecular environment in the solid or chemisorbed phase. Second, in the energy range 11-15 eV there is a high density of excited states: therefore, perturbation of these molecular Rydberg states by the surrounding medium in a condensed phase may partly shift oscillator strength to other excited states, but it is unlikely to shift oscillator strength significantly in energy.

## VI. Conclusions

On the basis of similarities between the SRS and ELS spectra of chemisorbed CO on Ni(111) and the ELS and optical absorption spectra of molecular CO, we have suggested interpretations of surface optical excitations involving (i) charge transfer transitions near 6 eV from the metal states to the CO ( $2\pi^*$ ) affinity level, (ii) singlet valence excitations  $X^1\Sigma^+ \rightarrow A^1\Pi$  of the chemisorbed molecule near 8 eV, and (iii) Rydberg transitions near 13-14 eV and above. However, we should caution that in principle any of the observed SRS or ELS structures could instead be related to chemisorption-induced changes in the surface optical response of the metal itself (metal  $\rightarrow$  metal transitions altered at the surface), and this possibility cannot be confirmed or discounted at present.

This first SRS investigation of the optical transitions of a chemisorbed molecule illustrates several experimental difficulties with the technique (e.g. significant noise and drift compared to the small total reflectance changes, the presence of second order and stray light contributions).

More importantly, it reveals several general problems with the study of electronic excitations of chemisorbed molecules by SRS or ELS: (i) relatively few spectral structures are resolved, and these are generally broad; (ii) the identification of valence optical transitions is difficult because neither initial nor final states of the transitions are known; (iii) the excitations of molecules above the first valence transitions are very complex; (iv) relatively few realistic theoretical calculations have been made for chemisorbed molecules, and these generally address only the ground state eigenvalues of the system (often only the filled states), but not its characteristic excitations; and (v) lineshape analysis in SRS and selection rule effects in both ELS and SRS may represent further complications. Perhaps the most encouraging aspect of the present results for CO chemisorption on Ni(111) is that the transitions associated with CO chemisorption show a definite correlation with the optical excitations of molecular CO and with the transition metal carbonyls.

## VII. Acknowledgement

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$\text{Si}(3s^2 3p^2) = 1.15$ . These 3s-3p radii are not much larger than the ground state  $\text{C}\equiv\text{O}$  bond length of 1.128 Å.

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Figure Captions

- Fig. 1. Schematic representation of the energy levels and optical excitations of the free and chemisorbed CO molecule.  $E_{\text{VAC}}$  and  $E_F$  represent the vacuum level and the metal Fermi level respectively. Arrows indicate valence (V) and Rydberg (R) excitations of the free and chemisorbed molecule as well as charge-transfer (CT) transitions between metal d-bands and adsorbate orbitals.
- Fig. 2. Spectra of relative reflectance changes caused by CO chemisorption on Ni(111) at 300 K. Solid curve: p-polarized spectrum obtained at  $50^\circ$  angle of incidence using synchrotron radiation; dashed curve above  $\sim 9$  eV: s-polarized spectrum obtained at near-normal incidence using synchrotron radiation; dashed curve below  $\sim 9$  eV: s-polarized result obtained at near-normal incidence using unpolarized light from a  $\text{H}_2$  discharge lamp.
- Fig. 3. Spectra of changes in the imaginary part of the surface dielectric function caused by CO chemisorption on Ni(111) at 300 K obtained by analysis of Fig. 2 for s-polarized light at near-normal incidence (dot-dash curve) and for p-polarized light at  $50^\circ$  angle of incidence (solid curve). Uncertainty in the magnitude of the peak intensity near  $\sim 6$  eV in the s-polarized spectrum is indicated by the dotted portion of the dashed curve.
- Fig. 4. Electron energy loss spectra for CO chemisorption on Ni(111) at 300 K, primary beam energy  $E_p = 250$  eV.
- Fig. 5. Optical excitation spectra of chemisorbed and free CO: (a) SRS spectra for chemisorbed CO/Ni(111), s- and p-polarized light, as in Fig. 3; (b) ELS difference spectrum for chemisorbed CO/Ni(111) as in Fig. 4; (c) ionization potentials for molecular orbitals of chemisorbed CO on Ni(111), with the ionization range for the  $5\sigma - 1\pi$  band in the photoemission spectrum shown as the shaded region and the peak of this band depicted by a vertical line; (d)

ELS spectrum for solid phase CO from Ref. 31; (e) ELS spectrum for gas phase CO from Ref. 31; (f) ionization potentials for gas phase CO.

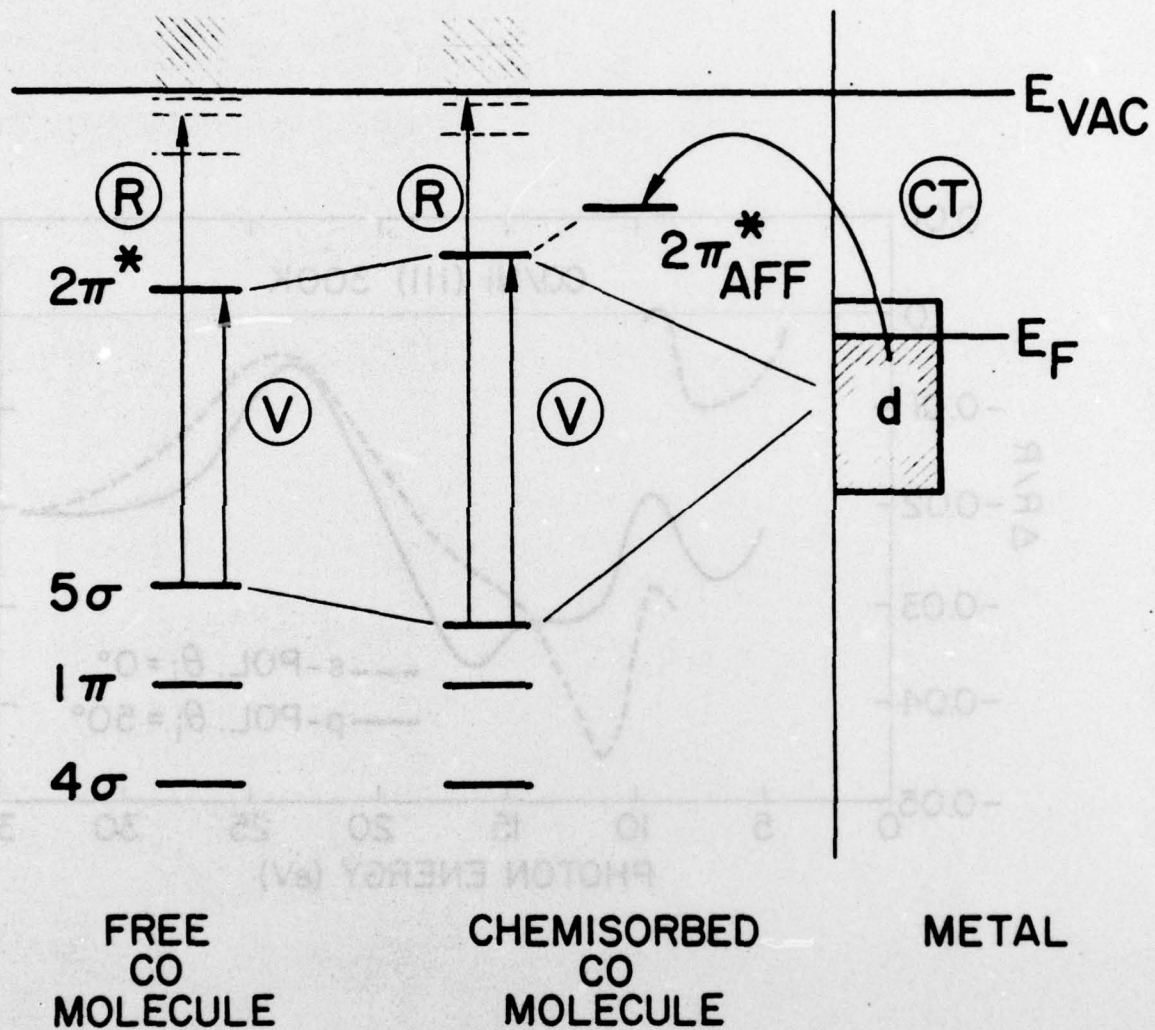


FIG. 1



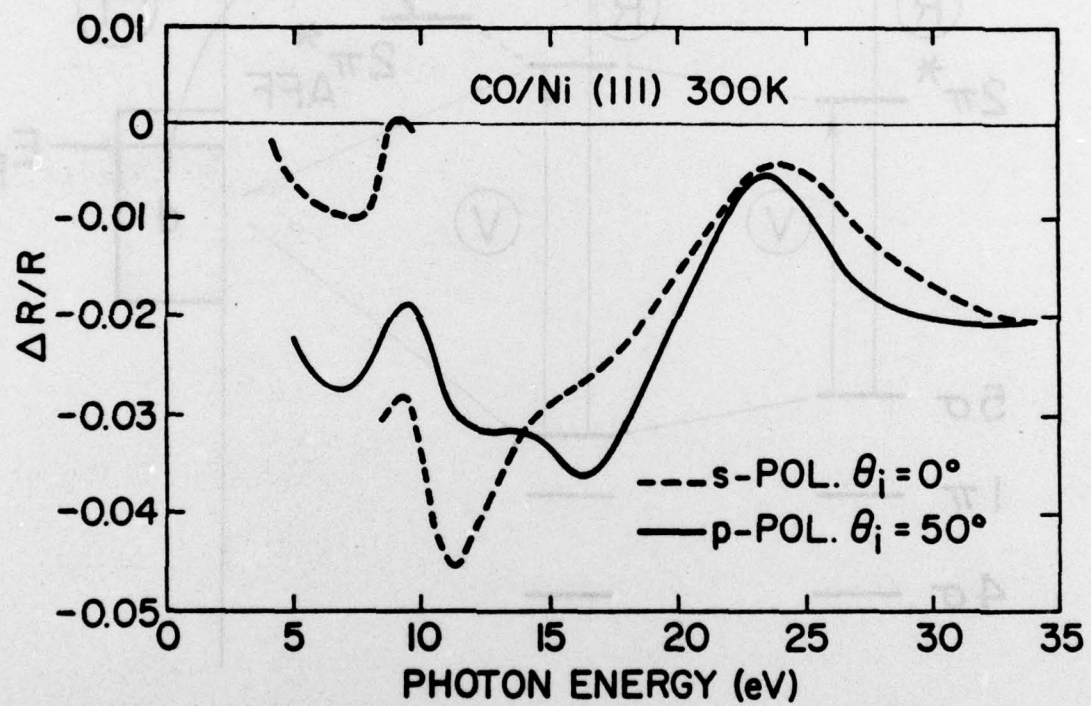


FIG. 2

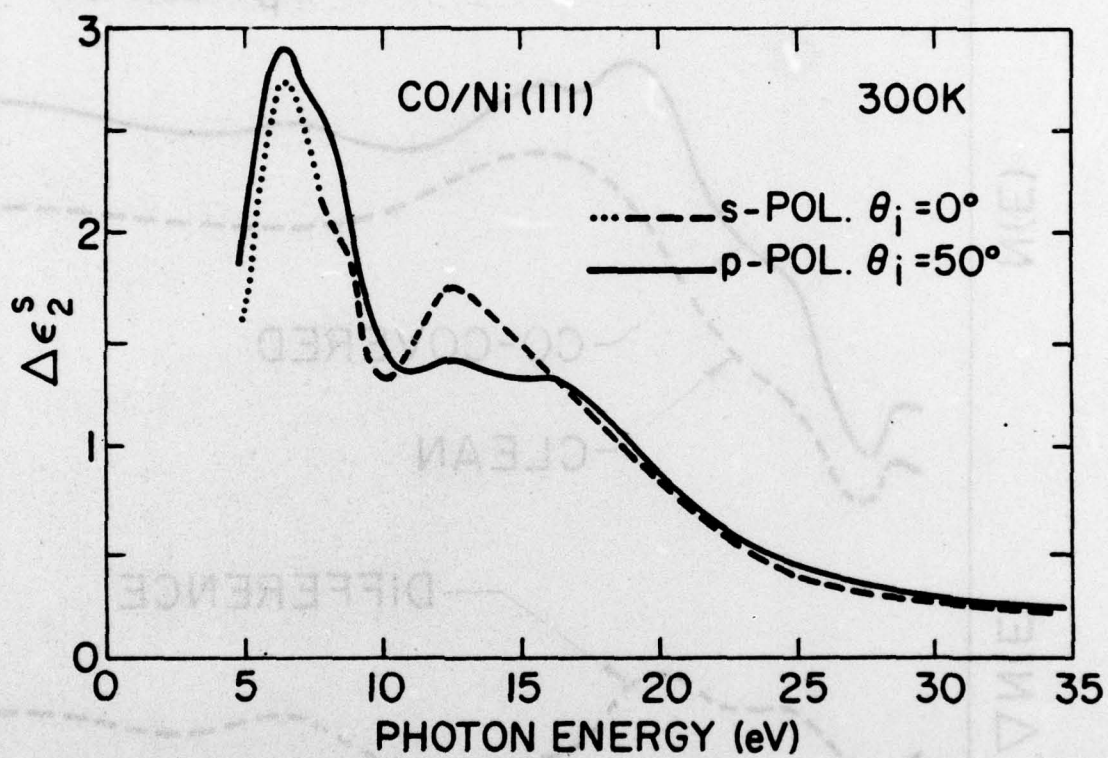


FIG. 3

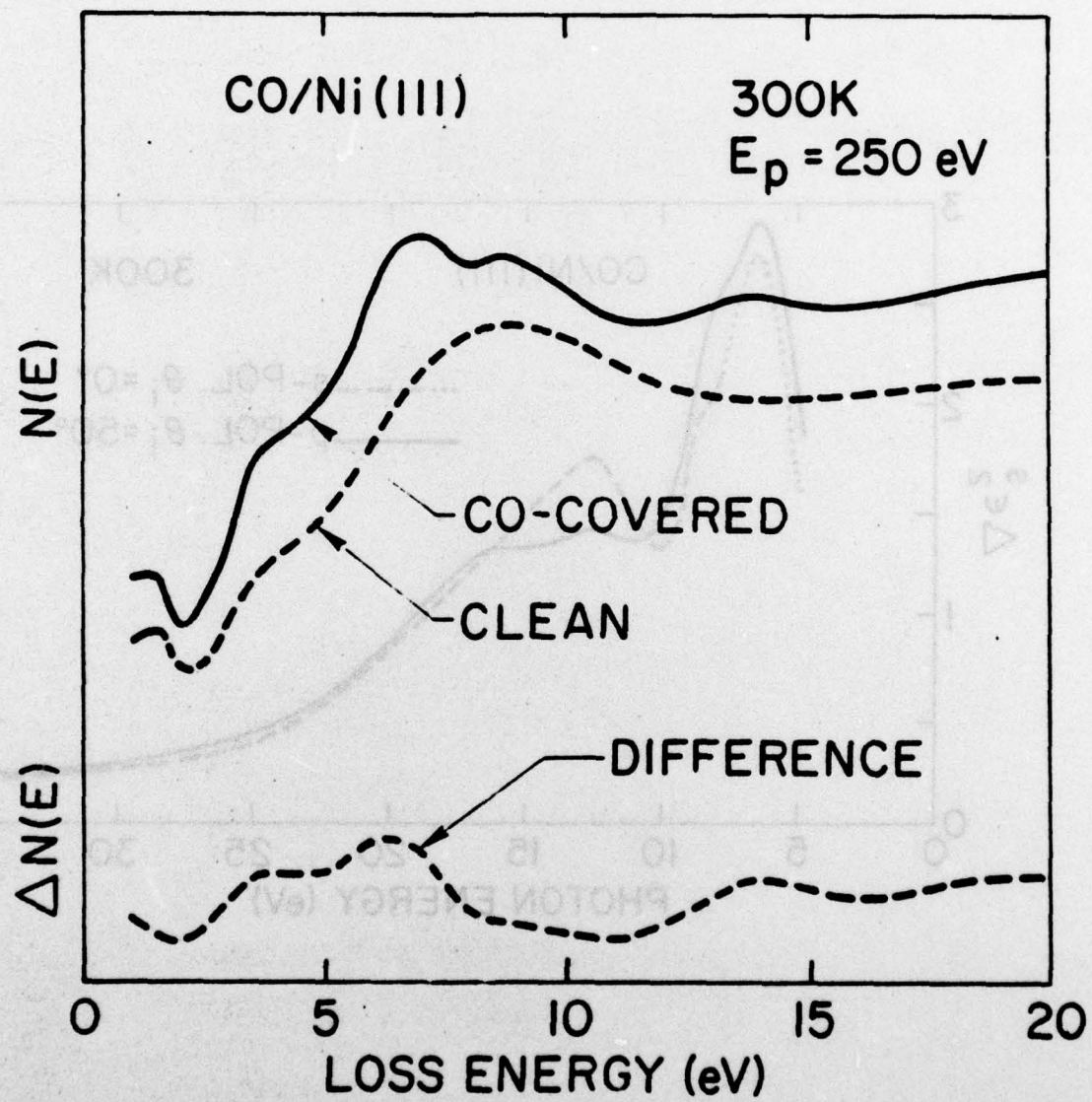


Fig. 4



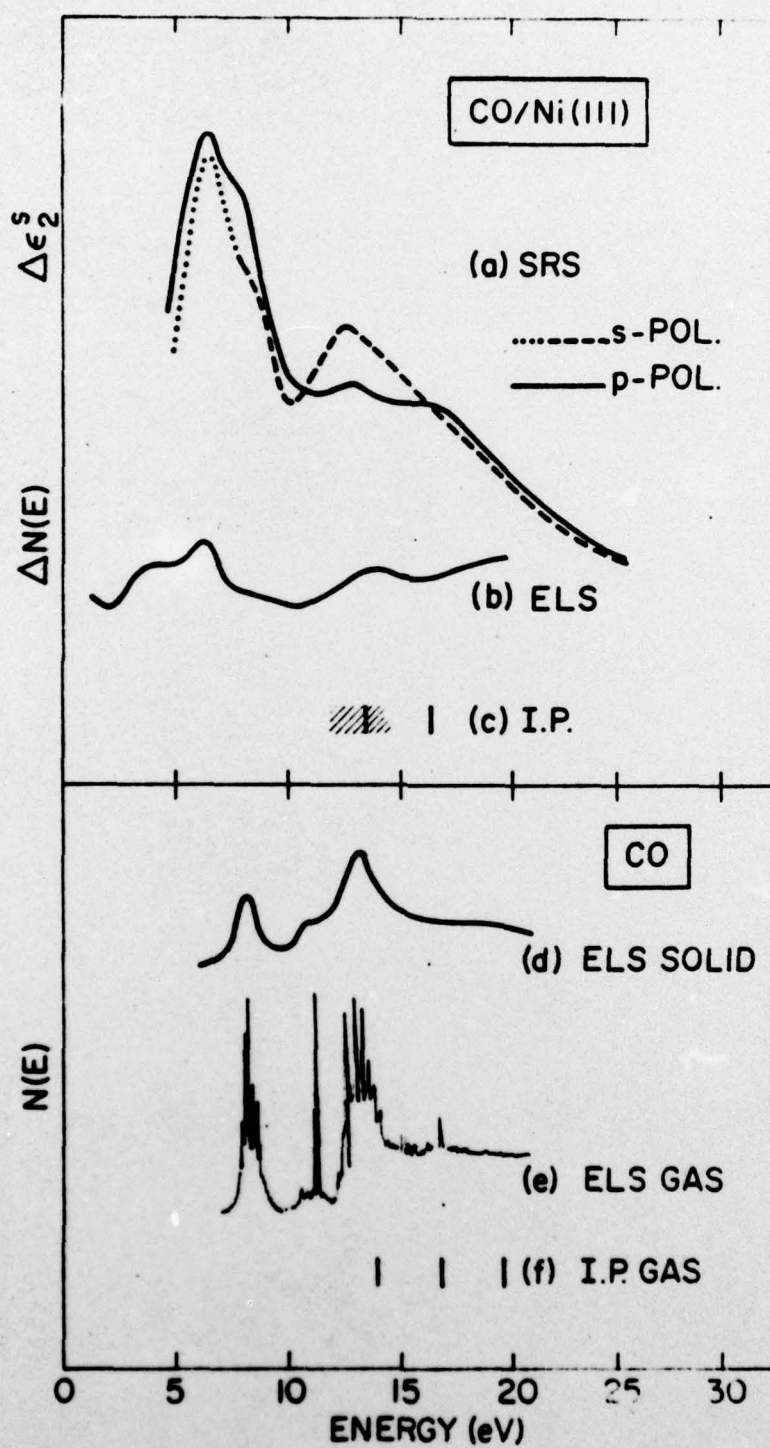


FIG. 5

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